MICROANALYSIS OF SIDEROPHILE ELEMENTS IN FREMDLINGE USING LASER ABLATION ICP-MS.

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Introduction: Laser ablation ICP mass spectrometry has been used to measure distributions of the highly siderophile elements Mo, Ru, Rh, Pd, W, Re, Os, Ir, and Pt in Fremdlinge with a spatial resolution of 15 µm. Variations among Fremdlinge in an Efremovka CAI show that Ru/Os and other PGE ratios were established in Fremdlinge prior to their incorporation into CAIs, and that these ratios are not always chondritic.

Fremdlinge are metal-rich assemblages, having high concentrations of refractory siderophile elements, found in CAIs. They are believed to have formed by early condensation of refractory siderophile alloys, subsequent reaction at lower temperatures to incorporate Fe, Ni, and P, and later oxidation and sulfidation [1, 2]. Condensation temperatures of Fremdling components, as indicated for example by the bulk Ru/Os ratios measured by neutron activation analysis, suggest that Fremdlinge within a single CAI may have had varying thermal histories [1, 2]. This interpretation is complicated by the possible effects of late-stage sulfidation on the PGE concentrations in Fremdlinge [3].

The present experiments allow comparisons of siderophile concentrations to be made not only between Fremdlinge but also within a Fremdling. Data are presented for four Fremdlinge from two CAIs in Efremovka (CV3-reduced), and from a sulfide vein in Allende (CV3-oxidized).

Experimental: The laser ablation system utilized a CETAC LSX-200 laser ablation peripheral with a Finnigan MAT Element ICP mass spectrometer [4, 5]. The isotopes monitored were ^{31}P, ^{34}S, ^{51}V, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{95}Mo, ^{101}Ru, ^{103}Rh, ^{105}Pd, ^{182}W, ^{187}Re, ^{192}Os, ^{193}Ir, ^{195}Pt, and ^{197}Au. Instrumental sensitivity factors for each isotope were determined by measuring signal intensity from the group IVB iron meteorite Hoba, which has known concentrations of the elements of interest [5]. Each point on the sample was analyzed by three successive five-pulse laser bursts; the laser-ablated pit produced was 15 µm in diameter and approximately 8 µm deep. Typical signal intensities for 800 ppm ^{193}Ir$^+$ were ~5000 cps, with a background of ~1 cps.

Results and Discussion: In Allende CAIs metal- and sulfur-rich veins appear to be associated with the Fremdlinge; in polished sections they are often observed in cracks that cross-cut Fremdlinge. Figure 1 shows a scan across a sulfide vein in an Allende CAI, TS68. Several elements, including Ru, Rh, and Os, show enrichment correlated with the presence of sulfur in this scan. The enrichment of Ru is greater than that of Rh and Os; other PGEs were not detected in the

vein (PGE detection limits were ~1 ppm in this analysis, except 8 ppm for Pd). The presence of these elements in the sulfide vein implicates sulfidation as a process that may have modified the original siderophile abundances of Fremdlinge subsequent to incorporation into the CAI. This possible compromise of Allende Fremdlinge led to subsequent study of Fremdlinge in Efremovka, where it was expected that original siderophile abundances have been better preserved.
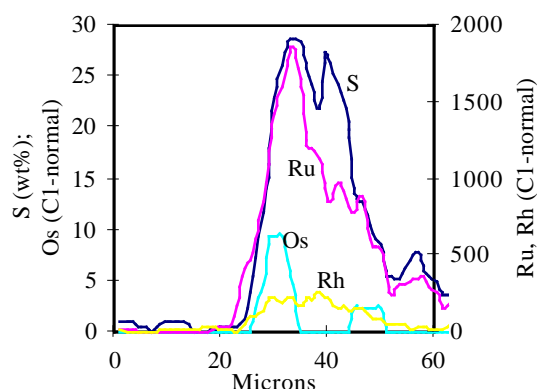

Figure 1. S, Ru, Rh, and Os across a sulfide vein in an Allende CAI. Note scales.

The abundances of siderophiles in a Fremdling in the Efremovka CAI Ef3 are presented in Figure 2, normalized to C1 chondrites [6] and shown in order of increasing volatility in a solar gas [1]. Each point in Figure 2 represents the mean and one standard deviation of measurements from five different points on the Fremdling. This Fremdling, described as The Heart [7], consists of a fine intergrowth of kamacite and taenite, with accessory vanadian magnetite present as 0.5-5 µm grains; each measurement sampled an unknown mixture of the three components. The relative abundances of Re, Os, Ir, Ru, Pt, and Rh are shown to be nearly chondritic in this Fremdling. Relatively volatile Pd, however, is strongly depleted. Note also the strong negative anomalies for W and Mo; these have been observed previously in Fremdlinge in Allende and were ascribed to late-stage oxidation and migration of W and Mo into the silicate host [2]. This interpretation is supported in the present analysis by bulk INAA data from this same CAI [8], represented by the lower curve in Figure 2; they display a similar pattern for Re and the PGEs, with W and Mo much less depleted in the bulk than in the Fremdling Ef3.

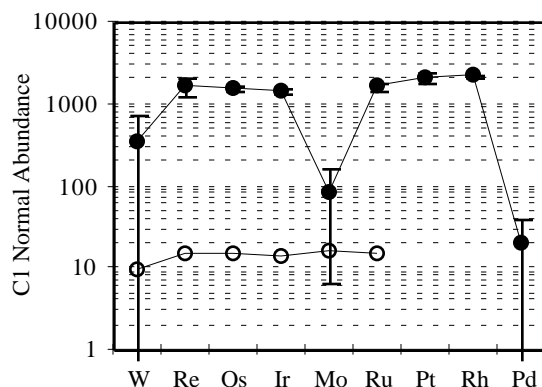SIDEROPHILE ABUNDANCES IN FREMDLINGE: A. J. Campbell et al.

Figure 2. Efremovka CAI Ef3. Filled circles: individual Fremdling [this study]; open circles: bulk CAI [8].

Abundance patterns for three separate Fremdlinge from the EF2 CAI in Efremovka [9] are displayed in Figure 3. Two of these Fremdlinge, EM1 and EM7, have essentially chondritic patterns (with the exception of the less refractory Pd), but EM2 has a pattern, including the Ru/Os ratio (0.55 x C1), that is distinctly volatile-depleted (Re/Pt = 2.6 x C1). These contrasting abundance patterns from individual Fremdlinge must have been established in the solar nebula, prior to their incorporation into the CAI. Subsequent processing was less extensive than that needed for homogenization of the metal inclusions.
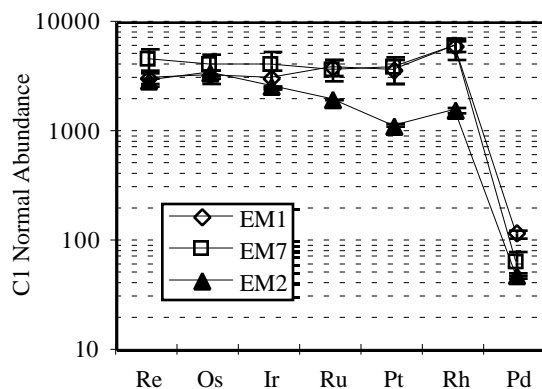

Figure 3. Fremdlinge in Efremovka CAI EF2.

A more detailed study of EM2 was also carried out (Fig. 4). This specimen consists principally of taenite (~55 wt% Ni), with accessory phases zoned concentrically within the ~350 µm diameter Fremdling. The interior of the Fremdling includes schreibersite grains (<10 µm) and smaller (<2 µm) Fe,Mo,W-bearing alloy grains, and the outermost rim,   30 µm wide, is composed strictly of taenite. In some places outside the rim there also exists an irregular shell of phosphate between the Fremdling and the surrounding silicate. The siderophile abundance patterns in the interior of the Fremdling are shown in Figure 4 to have a systematic enrichment anticorrelated with the volatility of the

elements. The rim shows a more complicated pattern; the heavy PGEs (Re, Os, Ir, Pt) are all lower than in the interior, while the light PGEs (Ru, Rh, Pd) have concentrations similar to those in the interior. The abundance pattern of the rim in relation to that in the interior is in close agreement with that which results from partitioning between schreibersite and metal phases in meteorites [10]. In a phosphide-rich Fremdling, we determined the following taenite / schreibersite concentration ratios: Ru = 0.9, Rh = 1.2, Pd = 1.5, Re   26, Os   290, Ir   200, Pt   43. Although there is no measurable phosphorus in the rim of EM2, the discrimination observed here between the heavy PGEs and the light PGEs is best explained through partitioning between the metallic interior of the Fremdling and a schreibersite layer occupying what is now the rim. The P in this postulated schreibersite may have been removed through later oxidation of the Fremdling, producing the outer phosphate layer now present and leaving a metallic rim with inherited PGE signatures.
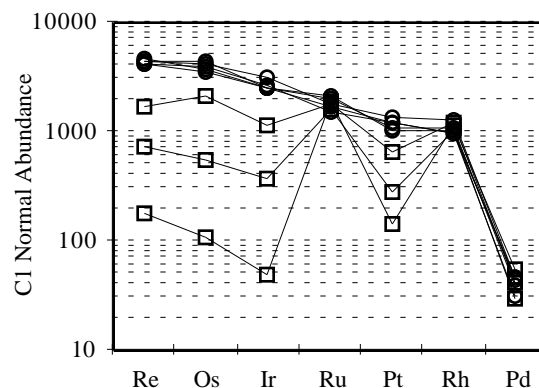

Figure 4. Fremdling EM2 in Efremovka CAI EF2. Circles: interior; squares: rim.

References: [1] Sylvester P. et al. (1990) *GCA, 54,* 3491-3508. [2] Palme H. et al. (1994) *GCA, 58,* 495-513. [3] Blum J. et al. (1989) *GCA, 53,* 543-556. [4] Campbell A. and Humayun M. (1999) *Anal. Chem.,* in press. [5] Campbell A. and Humayun M. (1999) this volume. [6] Anders E. and Grevesse N. (1989) *GCA, 53,* 197-214. [7] Casanova I. and Grossman L. (1993) *LPSC, XXIV,* 257-258. [8] Sylvester P. et al. (1993) *GCA, 57,* 3763-3784. [9] Fisenko A. et al. (1992) *Geochem. Int., 29,* 85-93. [10] Jochum K. et al. (1980) *Z. Naturforsch., 35a,* 57-63.